Nature of the incommensurate-paraelectric transition: A two-dimensional exchange-difference NMR study

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^{87}Rb two-dimensional exchange-difference NMR was used to study collective motions in the incommensurate (I) and paraelectric (P) phases of Rb_2ZnCl_4, which elucidate the nature of the I-P transition. We measured the cross-peak frequency displacement vs mixing time and observed a gradual increase towards an asymptotic value in the I phase but a sudden jump to the final value in the P phase. The P phase results are identified as normal modes arising from simultaneous displacement of the Rb ions and rotations of the $ZnCl_4$ between two sites, and these modes freeze out in the I phase to become the modulation wave.

Incommensurate (I) systems,[1,2] exhibit long-range order but no translational symmetry and can thus be regarded as intermediate between perfect crystals and glasses. These systems have at least two competing periodicities [that of the incommensurate modulation wave (or waves) and that of the underlying crystal structure] whose wave vectors are not rational multiples of one another.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are powerful techniques for elucidating the static and dynamic properties of the modulation wave in the I state. The static properties have been studied primarily by line-shape measurements[3–5] and the dynamic properties (i.e., those involving amplitudon and phason dynamics as well as diffusionlike motions of the modulation wave) by relaxation time,[6–10] Hahn spin-echo magnetization decay,[11–13] and two-dimensional (2D) exchange NMR studies.[14,15] A study of the paraelectric-incommensurate transition[1,2] is important in order to understand the mechanism for formation of the modulation wave and hence to understand the fundamental nature of the I phase. Our description of this transition is based on the soft-mode picture[16] in which the I modulation wave is a frozen normal mode from the paraelectric (P) phase.

In this paper we present the results of 2D exchange-difference NMR measurements[17] both in the I and in the higher-temperature P phase of the incommensurate insulator Rb_2ZnCl_4. Rb_2ZnCl_4 is paraelectric belonging to the orthorhombic space group P_{cmn}-D_{2h}^{16} above $T_1 \cong 302$ K, incommensurate between 302 and 192 K, and commensurate and ferroelectric ($C_{2\nu}^9$) below $T_C \cong 192$ K.[18] In both I and P phases we measured changes in the NMR spectra of ^{87}Rb due to motions associated with the modulation wave (in the I phase) or with its precursor (in the P phase). As a result of these measurements we can identify the P-phase normal modes as simultaneous displacement motion of Rb ions and corresponding reorientational motion of the $ZnCl_4$ tetrahedra between two sites. These motions freeze out and change into the modulation wave motions in the I phase.

An ideal impurity-free I system is characterized by the existence of a gapless phason (Goldstone) mode in which the I modulation wave moves through the crystal without friction. This theoretical prediction has not been observed in real I systems, which have discrete structure and impurities that pin the modulation wave. Due to thermal fluctuations, the pinning potential can be overcome so that the modulation wave can become temporarily depinned and mobile.[1,2] Since the pinning centers have a random spatial distribution and pinning strength, the thermal depinning is random, giving rise to a random diffusionlike character of the modulation wave motion.[11,12]

The 2D exchange-difference NMR technique[14,19] is a variant of the 2D exchange NMR technique[19] involving taking the difference between 2D exchange NMR signals at two different mixing times, one long and one as short as possible. The standard 2D exchange NMR technique can in principle detect any spatial motion of the resonant nucleus during the mixing time t_{mix} such that the Larmor frequencies at the beginning and the end of t_{mix} are different. It is most useful for studying dynamic processes which are too slow to affect the line shape. The static nuclei with unchanged resonance frequencies during t_{mix} contribute to the diagonal intensity ($|\nu_1| = |\nu_2|$) of the 2D spectrum $S(\nu_1, \nu_2)$. The 2D spectrum is a plot of the NMR intensity vs two frequencies, ν_1 and ν_2, whose values correspond, respectively, to the initial and final Larmor frequencies of the moving spins. The nuclei which jump during t_{mix} to other lattice sites where they have different resonance frequencies, however, create off-diagonal ($|\nu_1| \neq |\nu_2|$) peaks, called cross peaks. However, the standard 2D exchange NMR method is not applicable to situations where the frequency change due to motions is very small compared to the width of the continuous diagonal. The diagonal is continuous in the case of inhomogeneously broadened spectra (such as for I systems); its length is a measure of the inhomogeneous broadening and its width corresponds to the homogeneous linewidth originating from T_2 processes. In this case cross peaks will not be resolved from the continuous diagonal and hence cannot be observed or identified. The solution to this problem is to apply the 2D exchange-difference NMR technique.[14]

A 2D exchange-difference spectrum arises from only the moving spins, since the signal from the static spins is eliminated by subtraction. If we subtract the 2D exchange signal corresponding to the short (ideally zero) t_{mix} from the ex-

change signal corresponding to a longer t_{mix}, then the diagonal will have a negative intensity and will contrast to the cross peaks which will have a positive intensity. In this way, the cross peaks (arising from those spins that have moved during t_{mix}) can easily be distinguished from the continuous diagonal. This technique is, of course, limited to mixing times that are shorter than T_1; hence this limitation provides an upper limit to the slowness of the motion that can be detected at a given temperature. In our experiments this potential loss of signal for long t_{mix} is not a serious limitation since $T_1 \geq 8$ ms in both I and P phases, and the longest t_{mix} that we used was 7 ms. A second, potentially more serious, problem for short T_1 is that the difference signal involves subtraction of 2D spectra at different mixing times and can cause errors if the mixing times are comparable to T_1. To avoid this source of error, we used T_1 weighting (as described in Ref. 14) in all our measurements, so that the T_1 effects were the same for both the long and short t_{mix} 2D exchange signals.

Our 2D exchange-difference NMR experiments were performed at 116.15 MHz (8.45 T) on a Rb_2ZnCl_4 single crystal, by irradiating the ^{87}Rb central transition $\frac{1}{2} \rightarrow -\frac{1}{2}$ using the 12-pulse 2D exchange-difference sequence developed by Dolinsek.[14] All measurements were performed at a specific crystal orientation relative to the magnetic field ($\mathbf{a} \perp \mathbf{H}_o$, where $a > c > b$). In the P phase the Rb ions in a given unit cell can be divided into two inequivalent sets [Rb(1) and Rb(2)], and, at our orientation, each gives rise to a separate single NMR line. All measurements described in this paper were performed on Rb(2), since these Rb ions experienced a larger incommensurate broadening.

In the I phase we performed the 2D exchange-difference experiment at $T = 296$ K and at $T = 301.3$ K, which is very close to the I-P transition. The ^{87}Rb NMR absorption line is inhomogeneously broadened due to the second-order electric quadrupolar interaction arising from atomic displacements in the modulation wave. For Rb_2ZnCl_4, the ^{87}Rb spectrum is characterized by two peaks at the edge (called edge singularities[1]), and has a width of approximately 11 kHz at $T = 296$ K. The 2D exchange difference spectrum has a diagonal shape since the change in frequency during the mixing time is much smaller than the width of the 1D spectrum. Figure 1(a) displays the ^{87}Rb 2D exchange-difference spectrum for part of the I line shape (specifically, the part which includes the edge singularity closest to the excitation frequency). The change in frequency due to motions, measured as the horizontal (or vertical) distance from the diagonal to the cross peaks [Fig. 1(a)], was determined for different values of the mixing time. We increased t_{mix} until an asymptotic value of the frequency shift was obtained, which corresponds to the maximum distance traveled by the modulation wave. Note the continuous variation of the frequency shift with the mixing time shown in Fig. 1(b). This continuous variation corresponds to the progressive motion of the modulation wave, which moves only a very small fraction of its wavelength in each step. This observation effectively rules out many alternative models for the motion in this phase (e.g., random fluctuations due to two-site motions, librational oscillations, phason or amplitudon oscillatory motions, etc.),

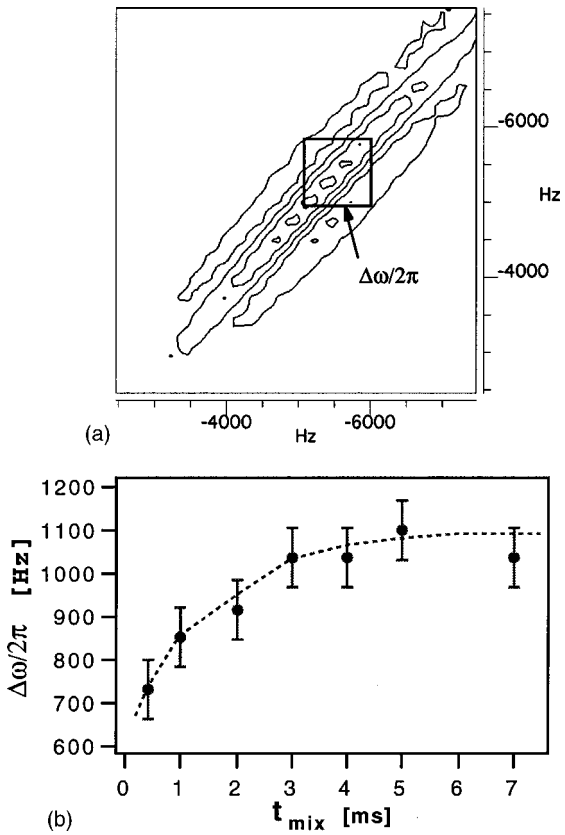

FIG. 1. (a) ^{87}Rb 2D exchange-difference spectrum for part of the *I* line shape (the edge singularity closest to the excitation frequency) at $T = 296$ K for $t_{mix} = 4$ ms. (b) The maximum change in the NMR frequency $\Delta\omega/2\pi$ due to the motion of the modulation wave, plotted as a function of the mixing time t_{mix} at $T = 296$ K.

since such motions would not give rise to the observed progressive displacements and would likely be too rapid to be observed in our 2D spectra.

The modulation wave displacement can easily be obtained from the cross-peak frequency shift in the 2D exchange-difference spectrum. For our crystal orientation, the NMR frequency has a linear dependence on the modulation wave amplitude,[1] given by $\omega(x) = \omega_0 + \omega_1 \sin(kx)$, where k is the modulation wave wave vector, $\omega_0/2\pi$ is the NMR frequency at the center of the I spectrum, and ω_1 is proportional to the modulation wave wave amplitude and corresponds to half the linewidth of the 1D I spectrum. The maximum modulation wave displacement X_{max} can then be determined from the asymptotic value of the measured frequency shift $\Delta\omega_{max}/2\pi$ using the formula

$$X_{max} = \frac{\lambda}{2\pi}\left\{ \arcsin\left(\frac{\Delta\omega_{max} + \omega(x) - \omega_0}{\omega_1} \right) - \arcsin\left(\frac{\omega(x) - \omega_0}{\omega_1} \right) \right\}. \quad (1)$$

Here λ is the modulation wave wavelength [$\lambda = 2.8$ nm for Rb_2ZnCl_4 (Ref. 1)]. This value is roughly equal to the **c** lattice constant in the *C* phase, which in turn is three times that in the P phase. We determined X_{max} at an NMR frequency that is ~ 1 kHz away from the edge singularity. At this frequency, we obtained values for X_{max} of 1.3 ± 0.3 Å at

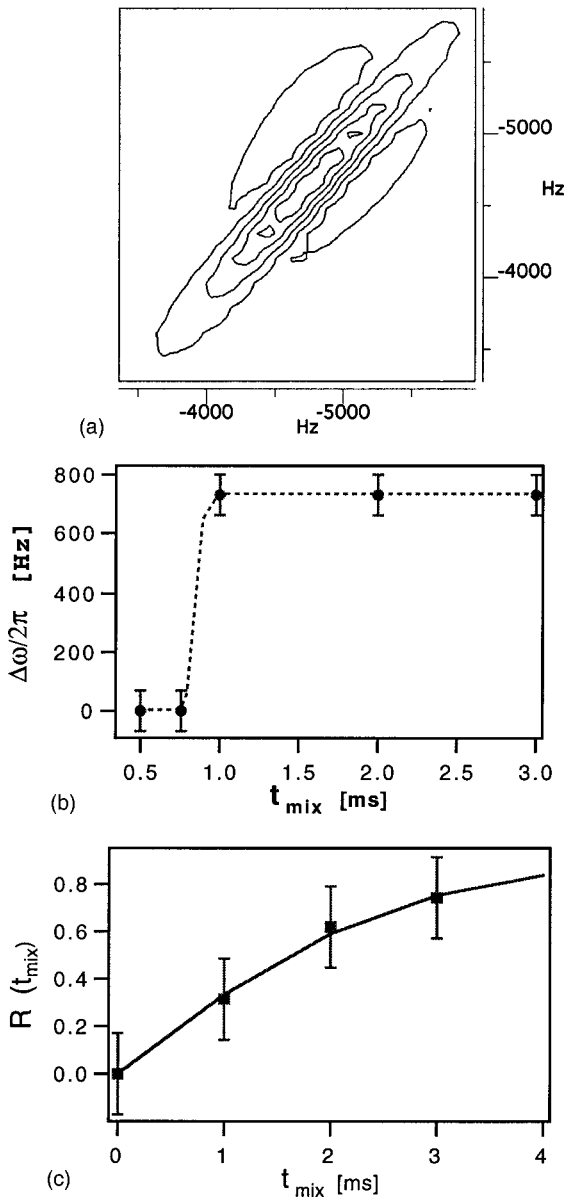

FIG. 2. (a) ^{87}Rb 2D exchange-difference spectrum at $T=326$ K in the P phase for $t_{\mathrm{mix}}=3$ ms. (b) The change in the NMR frequency $\Delta\omega/2\pi$ due to motions plotted as a function of the mixing time t_{mix} at $T=326$ K. (c) The ratio between the cross and diagonal peaks intensities $R(t_{\mathrm{mix}})$ as a function of the mixing time at $T=316$ K. The solid line is a theoretical fit using Eq. (2).

296 K and 2.1 ± 0.3 Å at 301.3 K. This result shows that at higher temperatures the modulation wave travels a greater distance due to its higher mobility resulting from thermal depinning. The slight discrepancy between our results and that in Ref. 14 ($X_{\max}=1.58$ Å at 291 K) likely reflects differences in impurity content (which probably varies slightly from sample to sample). X-ray measurements[20] report that the actual maximum atomic displacements in the modulation wave at 233 K are about 0.4 Å for the Cl and are even smaller ($\sim$0.1 Å) for the other atoms.

The situation completely changes in the P phase. We performed the ^{87}Rb 2D exchange-difference experiment at three different temperatures (316, 326, and 340 K), all well above the I phase, and observed that motions still exist. Figure 2(a) shows the ^{87}Rb2D exchange difference spectrum at 326 K. What is the most interesting is the variation of the frequency shift with the mixing time [Fig. 2(b)], which shows a *sudden* jump at a certain t_{mix} after which it remains constant. This behavior clearly suggests that motions now occur only between two sites.

Independent confirmation of this picture can be obtained by determining the variation with t_{mix} of the ratio of the *intensities* (rather than the displacements) of the cross and diagonal peaks. It has been shown[15,19,21] that, for a two-site motion, the ratio of the cross to diagonal peak intensities $R(t_{\mathrm{mix}})$ in a standard 2D exchange spectrum is

$$R(t_{\mathrm{mix}})=A\tanh\frac{t_{\mathrm{mix}}}{\tau_{\mathrm{exch}}}, \tag{2}$$

where $A\leqslant 1$. (The constant A equals unity for a symmetric double well potential and is less than one for the asymmetric case.[15]) We may interpret τ_{exch} as the correlation time of the motion. However, in our experiment the cross peaks are not resolved from the continuous diagonal in the simple 2D exchange data; nevertheless, we can still obtain this information since we have generated both the 2D exchange and the 2D exchange-difference spectra.

Figure 2(c) shows the variation of $R(t_{\mathrm{mix}})$ with the mixing time at $T=316$ K. From a fit to Eq. (2) we determined the correlation time τ_{exch}. The correlation time measured in this way was observed to decrease slowly from $\tau_{\mathrm{exch}}\cong 2.6\pm0.2$ ms at 316 K to $\tau_{\mathrm{exch}}\cong 1.8\pm0.2$ ms at 326 K to $\tau_{\mathrm{exch}}\cong 1.3\pm0.4$ ms at 340 K. Assuming thermally activated motion for which $\tau_c=\tau_0\exp(E_a/kT)$, we can estimate the activation energy to be roughly $E_a\cong 0.1$ eV. The smallness of the activation energy suggests that the motions may be correlated rather than due to single-ion hopping.

The two-site motion observed by us in the P phase is strongly supported by structural analyses performed with neutron scattering[22] and with x-ray diffraction,[20,23] which reveal that there exist two possible orientations of the $ZnCl_4$ tetrahedra that are occupied with equal probabilities. The distances separating the equilibrium positions of the Cl ions in these two orientations have been found by x rays[23] to be between 0.22 and 0.48 Å for different Cl ions. A model calculation[24] of the second-order quadrupolar shift of the Rb central transition shows that the reorientational motions of the $ZnCl_4$ groups *without* corresponding motions of the Rb ions would result in a much smaller frequency displacement ($\sim$15 Hz) than that observed by us ($\sim$400–500 Hz). However, a displacement of the Rb ions by as little as 0.01 Å can easily account for our observed frequency displacements.[24] Thus we conclude that the two-site motion observed in the P phase consists of reorientational motions between two equilibrium positions of the $ZnCl_4$ groups and accompanying small Rb motions between two sites.

In the I phase, the modulation wave motion originates from *progressive* misorientations of the $ZnCl_4$ tetrahedra and, as in the P phase, corresponding small displacements of Rb ions. A comparison of the behavior in the I and P phases thus suggests that the P-phase displacements simply become the I-phase modulation wave.

It may be surprising, at first glance, that the exchange-difference spectra show resolved cross peaks corresponding to the two sites, even though such peaks are not observed in

the 2D diagonal or in the 1D line shape. Our 2D *exchange-difference* spectrum, however, shows that the sites are separated by only 400–500 Hz (measured from the diagonal to the top of the cross peaks), which is less than our measured full width at half maximum (FWHM) of the 1D line ($\cong$1.2 kHz). The fact that these lines can be resolved in the *difference* spectrum proves that *slow* jumping was occurring between the sites.

Another surprising feature is that the frequency shift of the cross peaks in the P phase [Fig. 2(b)] is somewhat less than that in the I phase [Fig. 1(b)]. One would naively expect that an atom in the P phase would undergo a displacement corresponding to the maximum change in position of the atoms in the I phase. Since the modulation wave displacement ($X_{\max}$) is only a small percentage of its wavelength (λ), the corresponding frequency shift should then be less than in the P phase, if one neglects the temperature dependence of the modulation wave amplitude. However, the modulation wave amplitude (and thus the frequency gradient) has been shown[1] to decrease with increasing temperature as the temperature is raised in the I phase. Furthermore, the inhomogeneous linewidth, which is a measure of the modulation wave amplitude in the I phase, is roughly ten times larger at $T = 296$ K than that in the P phase, thereby implying a much larger frequency gradient in the I phase. Thus it is really not surprising that the cross-peak displacement is somewhat lower in the P phase than in the I phase.

In summary, we used 2D exchange-difference NMR to study ultraslow motions in Rb_2ZnCl_4, and we found that the cross-peak frequency displacements vs mixing time undergo a gradual change in the I phase but a sudden change in the P phase. We observed in the I phase a diffusionlike motion of the modulation wave between pinning centers and in the P phase a two-site correlated motion. We identified the two-site correlated motion in the P phase as reorientation of the $ZnCl_4$ groups and correlated Rb displacement. We further identified this motion to be the soft mode that freezes in the I phase and changes to a diffusionlike sliding of the modulation wave in order to regain the lost translational symmetry.

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